JAPANESE [JP,2002-037614,A]

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the filament shape carbon formed under hydrothermal-reaction conditions.
[0002]
[Description of the Prior Art]Carbon nanotube[S. Iijima, MRS Bull.19, and 43-49 (1994)] are one of the exotic materials with the highest attention degree in which a possibility of being used in new art and device from now on is high, and it inquires now, and composition is tried. In particular, it is a multiwalled carbon nanotube. (MWNT) Those sizes are changed in the broad range and they are a composite and a hydrogen storage body. [P.Chen, X.Wu, J. Lin, KL.Tan, Science285, 91-93 (1999)] Nano actuator[R.H. Baughman, et al., Science284, and 1340-44 (1999)] And a nano rod / template for nanowireIt is interesting at the point which enables various application containing [P.M.Ajayan,

Drawing selection Representative draw

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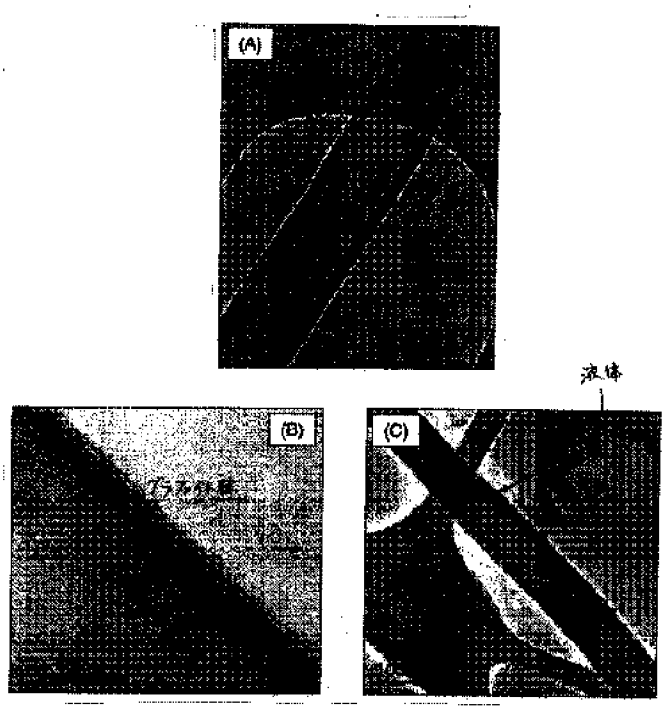

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O.Stephan, P.Redlich, C.Colliex, Nature375, and 564-567 (1995)]. The multiwalled carbon nanotube will be used also the next-generation electronic nano device. [S.Saito, Science278, and 77-78 (1997)] .Electronic and unique combination of a mechanical property of a nanotube [P. Poncharal, Z.L. Wang, D. Ugarte, W.A.d. Heer, and Science283-1513-1516 (1999)] ** and a nanotube are made attractive for a micro electronic-mechanical system (MEMS). [O. Inganas, I.Lundstrum, and Science284-1281-1282 (1999)] .

[0003]However, production of MWNT is troublesome and includes processes which are not environment-friendly, such as an elevated temperature. [D.T.Colbert, et al., Science266, and 1218-1222 (1994)] .Since yield at present is very low, those raw materials are dramatically expensive. In order to realize application potential of a carbon nanotube, raise yield and a manufacturing cost is reduced, and synthetic art must be improved so that it may become controllable [which it was / rather than / excellent to the geometric property (shape length, a diameter, and wall thickness) of a nanotube].

[0004]At present, the carbon arc electric discharge method is used most widely. The nanotube produced by this method is oxidation under control. [P.M. Ajayan, et al., and Nature362,522-525 (1993)] Or a wet chemicals method It is necessary to purify by [S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, and Nature372,159- (1994)]. However, an elevated temperature, an electric field, evaporation, and vacuums are not the indispensable conditions for producing a carbon nanotube. Electrochemical composition of the carbon nanotube succeeded in a comparatively low temperature (600 **) in the melting LiCl. [W.KHsu, et al., and Nature377,687 (1995)] .

[0005]The hydrothermal synthesis of a substance has many advantages compared with other methods. That is, hydrothermal synthesis is environment-friendly and cheap, enables reduction of the free energy for various balances, and enables composition of the phase which is not stable under other conditions. Supercritical water brings about the high compressibility which enables easy change of high diffusibility, the degree of low viscosity which makes mass transport easy and density, and solvent power rather than being able to set to a different chemicals phenomenon under a pressure, and a liquid state. [M.Siskin, R.Katritzky, Science254, and 231-237 (1991)] .As discovered by this invention person, covering of amorphous carbon can form in high voltage high temperature hot water. [Y and G.Gogotsi,

M.Yoshimura, Nature367, and 628-630 (1994)] .Then, the hydrothermal synthesis of the diamond was reported. [X.-Z. Zhao, R. Roy, KA. Cherian, A. Badzian, Nature385, and 513-515 (1997)] .It can generate under the pressure (10-100 MPa) which is a degree the temperature (> 200 **) in which formation of hydrothermal carbon is comparatively low, and middle. If [Y, G. Gogotsi, M. Yoshimura, Nature367, and 628-630 (1994)] are taken into consideration, it will seem that this method is very effective. Hydrothermal synthesis of a carbon filament Arrangement to which it is [on a substrate] good and [Y.G. Gogotsi, KG. Nickel, Carbon36, and 937-942 (1998)] were equal [Y, G. Gogotsi, and "nano structure carbon covering" G.-M. Chow, Ed., "NATO ARW about a nano structure film and covering", Santorini, Greece (Kluwer, Dordrecht, 1999) The potential of the hydrothermal synthesis about growth of a complicated carbon structure including issue] was proved. However, those filaments were thicker than general MWNT including the blank of periodic conical shape. [Y.G. Gogotsi, KG. Nickel, Carbon36, and 937-942 (1998)] .

[0006]Fullerene[Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. &Smalley, R. E. "C_{60}:book minster fullerene (Buckminsterfullerene)", Nature318, 162-163. (1985)] (And a fullerene related substance, for example, a nanotube) Since [Iijima, S., "the ******** micro small tube of graphite carbon", Nature354, and 56-58 (1991)] had many applicable fields, they charmed the interest of the researcher in the world greatly. Since it has high peculiar intensity and high peculiar rigidity, the carbon nanotube is considered in the use as a reinforcing fiber. "[Rao, C. N. R., Seshadri, R., Govindaraj, A. & Sen, and R. Fullerene, The structure of a nanotube, an onion, and related carbon", Mater. Sci. & Eng. R-Reports 15, and 209-262 (1995)] .Those substances are dramatically more useful still also in a next-generation electronic nano device. [Collins, P. G., Zettl, A., Bando, H., Thess, A. & Smalley, R. E. "nanotube device", Science278, and 100-103 (1997)] The template an inorganic nanotube / for other nanowire [Ajayan, P. M., Stephan, O., Redlich, P. & Colliex, C. "carbon nanotube as a metallic-oxide nano composite and a removable template for nano structures", Nature375, and 564-567 (1995)] Hydrogen storage body [Chen, P., Wu, X., Lin, J. & Tan, K. L. "high ingestion of ambient pressure and H_2 according to the alkali pouring carbon nanotube under the temperature of a degree middle", Science285, 91-93 (1999)] Nano actuator [Baughman and R. H. et al. "carbon nanotube actuator" Science284-1340-44 (1999)] The use as **** can be considered. Energy

generation, a catalysis, a superconductor, a photoconductor, an optical limiting circuit, etc. are contained in the applicable field of fullerene. "[Rao, C. N. R., Seshadri, R., Govindaraj, A. & Sen, and R. Fullerene, The structure of a nanotube, an onion, and related carbon", Mater. Sci. & Eng. R-Reports15, and 209-262 (1995), Dresselhaus, M. S. & Dresselhaus, G. "fullerene [as an electronic industry material], and fullerene derivation solid", and Ann. Rev. Mater. Sci.25, and 487-523 (1995)] .The possibility of the new generation with the characteristic and the use which are not known yet of a fullerene base compound is doing research of the fullerene base the much more attractive thing. [Tenne, R. "fullerene Mr. structure [containing an injected impurity and a heteroatom] and nanotube", and Adv.Mater.7,965-995 (1995)] .Therefore, many researchers search for the fullerene and the nanotube by which it is generated naturally, and it is not surprising things these to have pursued the synthetic art of the low-temperature low cost for new carbon substance generation. Fullerene is an arc process, for example. [Kratschmer, W., Lamb, L. D., Fostiropoulos, K. & Huffman, and D. R. "neomorphism of solid C_{60}: carbon" Nature347 and 354-358 (1990)] Pulse

form laser or convergence sunlight, carbonaceous direct induction heating, or hydrocarbon flame that sends soot [Creation" of Lieber, C. M. & Chen, C. C. "fullerene, and a fullerene base substance, Solid State Phys.48, and 109-148 (1994)] In **** and a nature, it is compoundable under the rarely produced extreme conditions. Production of a carbon nanotube is a carbon arc electric discharge method especially. [Ebbesen, T. W. & Ajayan, P. M. "large-scale composition of a carbon nanotube", Nature358, 220-221 (1992), Ebbesen, T. W. "carbon nanotube", and Ann. Rev. Mater. Sci.24, 235-264. (1994)] Vacuum evaporation of carbon [Ebbesen, T. W. "carbon nanotube", Ann. Rev. Mater. Sci.24, and 235-264 (1994)] And the catalyst or plasma decomposition of an organic compound "[Rao, C. N. R., Seshadri, R., Govindaraj, A. & Sen, and R. Fullerene, The structure of a nanotube, an onion, and related carbon", Mater. Sci. & Eng. R-Reports15, and 209-262 (1995)] It can attain "Be alike." All of such art need an elevated temperature (it is at least 1000 ** at at least 700 ** - 800 ** and fullerene with a nanotube), a vacuum system, a gas stream, and complicated apparatus. Yield is comparatively low and output needs purification. From these reasons, production of a carbon nanotube and fullerene is still expensive, and is not environment-friendly.

[0007]In the fullerene generated naturally, it is struck by

lightning, for example. [Daly, K., T. Buseck, P. R., Williams, P. & Lewis, C. F. "fullerene from ******", Science259, and 1599-1601 (1993)] The shock of a meteorite [Becker, L. et al. "fullerene in the Sudbury shock structure of 1,850 million years ago", Science265, and 642-645 (1994)] And wildfire [Heymann, D., Chibante, L. P. F., Brooks, R. R., Wolbach, W. S. & Smalley, R. E. "fullerene in the boundary layer of the third Cretaceous", Science265 and 645-647 (1994)] **** -- it has been discovered with a quantity slight in the rock exposed under the extreme condition. Existence of the fullerene to which the SHUNGA stone which is rock with much carbon content without the proof exposed under the extreme condition was reported [Buseck, P. R., Tsipursky, S. J.& Hettich, R. "fullerene from geological environment", Science257, and 215-217 (1992)] were not checked by other researchers. [Ebbesen, T. W. et al. "origin of the fullerene in rock", Science268, and 1634-1635 (1995)] .It seems that such geologic study agrees with the result of the laboratory experiment which shows that it can form only in the energy process that a fullerene molecule is very expensive well. However, the action of the fullerene under geological conditions is what began to be checked very very much by the latest research, and since it has not inquired broadly yet, such a conclusion may be wrong. Fang et al.[Fang and P. H. et al. "fullerene discovered in pit in China Yunnan" Innov. Mater. Sci.1 and 129-134 (1996)] discovered fullerene in Chinese coal. These days, Osawa et al. It is reported that a carbon nanotube exists in coal and carbonaceous rock [finishing [Osawa, E. et al. "observation of the fullerene in coal and carbonaceous rock, a carbon nanotube, and a nano particle", Nature, and presentation] (1999)].

[0008]The carbon nanotube is already compounded by the electrolysis in fused salt. [Hsu, W. K. et al. "condensed phase nanotube", Nature377, and 687 (1995)] .Amorphous carbon [Gogotsi, Y. G. & Yoshimura, M. "formation of the carbon film on carbide under hydrothermal-reaction conditions", Nature367, and 628-630 (1994)] And a diamond [Zhao, X. Z., Roy, R., Cherian, K. & A. Badzian, A. "hydrothermal-reaction growth of the diamond in a metal-C-H_2O system", It is also shown that Nature385 and 513-515 (1997)] can produce under hydrothermal-reaction conditions. Arrangement to which it is [on a substrate] good and the hydrothermal synthesis of the carbon filament was equal [Gogotsi, Y. G. & Nickel, K. G. "formation of the filament shape carbon from paraformaldehyde under an elevated temperature and high voltage", It was proved that it

had possibilities including Carbon36 and 937-942 (1998)] of growing up carbon structure with complicated art of hydrothermal synthesis. However, those filaments were thicker than the common carbon nanotube including the blank of periodic conical shape. [Gogotsi, Y. G. & Nickel, K. G. "formation of the filament shape carbon from paraformaldehyde under an elevated temperature and high voltage", Carbon36, and 937-942 (1998)] .The strong point of the hydrothermal synthesis in substance processing [Eckert, C. A., Knutson, B. L. & Debenedetti, P. G. "supercritical fluid as chemicals and a solvent for substance processing", Nature383, 313-318 (1996), Yoshimura, M. & Byrappa, K. "hydrothermal art for crystal growth and substance processing", (Andrew Williams and Noyes Inc., New Jersey, U.S., 2000) Issue] And it can produce at temperature (> 200 **) with low hydrothermal carbon. If [Gogotsi, Y. G. & Yoshimura, M. "formation of the carbon film on carbide under hydrothermal-reaction conditions", Nature367, and 628-630 (1994)] are taken into consideration, It seems that the method of hydrothermal synthesis is very promising about composition of fullerene and/or a carbon nanotube. The information about formation / stability / decomposing condition of the carbon allotrope in which research of the new hydrothermal action of a carbon allotrope is very important for the geologists who are searching for natural burying of those substances will be brought about.

[0009]

[Problem(s) to be Solved by the Invention]Since these carbon materials have many applicable fields, composition of the high yield in fullerene, and existence of natural burying of a carbon nanotube and its low temperature is a scientific very important technical problem. Until now, the above-mentioned carbon material was produced under extreme conditions, and the compounded output needed to be purified. Very little fullerene and nanotubes are only found in the nature.

[0010]The purpose of this invention is to provide filament shape carbon. Another purpose of this invention is to compound a nanotube from a hydrothermal C-O-H fluid under existence of a metal catalyst.

[0011]

[Means for Solving the Problem]being based on hydrothermal synthesis which is a new method -- 500 to 900 ** temperature -- desirable -- 700 to 800 **, and a pressure -- in 60-100MPa 30 to 200 MPa preferably, By using a mixture of polyethylene/water under existence of nickel, a closed carbon nanotube which has an open end was obtained

by multilayer structure. A nanotube which has the wall thickness of 100 carbon layers from some was generated. As an important feature of all the hydrothermal nanotubes, it has the small wall thickness of a 20 to 500 nm big inside diameter which is about 10%. This feature makes a hydrothermal nanotube a promising candidate in a future who is micro and can use for piping of a nano fluid device. Laser can cut a nanotube to desired size. The Raman microspectroscopic analysis of a single nanotube presents microcrystal graphite structure which agrees with high resolution TEM where it gathered well. It is proved [nanotube / which was observed under existence of a Ni particle / high-concentration] that hydrothermal synthesis is promising although a lot of multilayer nanotubes for various kinds of applicable fields are produced by low cost. Production of a nanotube under hydrothermal-reaction conditions has suggested that a nanotube may exist in coal formed under hydrothermal-reaction conditions, or a natural graphite burying layer.

[0012]Since these carbon materials have many applicable fields, composition of high yield in fullerene, and existence of natural burying of a carbon nanotube and its low temperature is a scientific very important technical problem. Until now, the above-mentioned carbon material was produced under extreme conditions, and compounded output needed to be purified. Very little fullerene and nanotubes are only found in a nature. Here, in a geological environment of temperature between 200 ** and 800 **, and a pressure of 100 or less MPa, an action of C_{60} according to an absence and existence of nickel under general hydrothermal-reaction conditions is described. The stability of C_{60} and the range of decomposition under existence of a hydrothermal fluid were checked, and formation of a carbon nanotube under existence of a nickel particle was shown. A result of research by this invention person explains existence of a natural carbon nanotube in a field of earth crust of the earth influenced by a hydrothermal-reaction system, and an absence of fullerene in rock exposed to a hot aquosity fluid.

[0013]Main point of this invention is in filament shape carbon formed under hydrothermal-reaction conditions. Said filament shape carbon is a closed carbon nanotube which has an open end by multilayer structure. Said nanotube is generated by wall thickness of 100 carbon layers from some.

[0014]Said nanotube has the small wall thickness of a 20 to 500 nm big inside diameter as an important feature which is about 10%. Said nanotube presents microcrystal graphite structure which agrees with high resolution TEM where it

gathered well, by the Raman microspectroscopic analysis.
[0015]Said hydrothermal-reaction conditions are given with a mixture of polyethylene/water. Said hydrothermal-reaction conditions are given with a mixture of the polyethylene/ water under existence of nickel. said hydrothermal-reaction conditions -- 500 to 900 ** temperature -- desirable -- 700 to 800 **, and a pressure -- 30 to 200 MPa, it is 60-100MPa preferably and is given with a mixture of the polyethylene/ water under existence of nickel.
[0016]
[Embodiment of the Invention]Example 1 fruit **: It can use in the form which mixed with a pure chemical or water various kinds of substances having contained carbon, and the suitable field of a C-O-H constitutional diagram (drawing 1) can be obtained. It is [handling / convenience] usable in polymer (for example, polyethylene) as a carbon source with the low cost for quick formation of a C-H-O fluid, and equilibration. Much experimentation was performed in University of Illinois of the U.S. Chicago state.
[0017]About the sample of polyethylene (PE), they are a three to 5 mm diameter, and ten to 50 mm length in deionized water. It put in in Au capsule. The quantity of water was changed up to 0 to 10 of the weight of polyethylene times. 3% Ni metal powder was added in the capsule. This is because it is known that iron-group metal will act as a catalyst of the growth from the gas phase of a nanotube. The capsule was heated under the pressure of the distilled water to 200MPa within the Tuttle Books (Tuttle) type tubular container made from Stellite superalloy. In processing of this example, 2 to 170 hours held temperature at 700 ** - 800 **.
[0018]A presentation and structure of the nanotube were investigated using the Raman spectroscopic analysis which is the easiest and most powerful technique for identifying a carbon allotrope, and an electron microscope. Renishaw 2000 [provided with Ar ion laser (excited wavelengths of 514.5 nm)] The Raman microspectroscope was used. Used TEM was JEOL 3010 (300 kV) which has lattice resolution of 0.14 nm (point resolution of 0.17 nm). Magnification 500,000 JSM-6320F up to twice was used as field emission SEM (FESEM). If this device is used, the high resolution in low acceleration voltage is possible by that object lens design. Furthermore the microscope was equipped also with the Noran Voyager EDX system including a light element X-rays detection analyzer, and this was used for the ultimate analysis of the nanotube. Distributed MWNT in acetone or toluene, and it was made to adhere on a Si wafer or the polished aluminum sample holder in the analysis using

Raman and FESEM, and was made to adhere on a race-like carbon grid in TEM analysis.

[0019]join ** :P it sets to the hydrothermal-reaction experiment using E -- MWNT was found out in an abundant quantity (drawing 2). The wall in which obtained MWNT generally contains the fringe up to 70 pieces (it had wall thickness (25 nm), an outer diameter up to 30 to 200 nm, and an inside diameter up to 160 nm.) On the other hand, in a series of another experiments, the tube which has about 10% of wall thickness of a diameter of 500 nm and this diameter was obtained. The ratio of a diameter versus length amounted to hundreds (to 50 mm). (Drawing 2) and most have closed the tube from the tip to the end in hollow, and the part had opened it wide. That is, the hydrothermal reaction MWNT was not only generable, but in this example, MWNT which has among known the greatest inside diameter / wall thickness ratio that can be proved was obtained (drawing 2).

[0020]The relation which the tube to a nickel particle is obvious, or was consistent was not accepted. Only very few nanotubes contained nickel nano particle at the tip. Some tubes presented the open end which has a tapered shape wall, and the number of fringes was decreasing even on five visible fringes through the whole (drawing 2 B). In some cases, the lattice fringe inclined to the vertical axis of a tube, and having RASEN nature was shown.

[0021]Drawing 3 shows the Raman spectrum of the single nanotube by which separation generation was carried out on the Si wafer. Although the appearance diameter of the diffraction limit was about 1 micrometer, MWNT of the diameter of NANOMETA was able to be seen on all the surfaces of a wafer by 1000 times in spite of the actual diameter. As a remarkable feature of this spectrum, the primary band which has a shoulder belt in about 1620 cm^{-1} is included in about 1580 cm^{-1}. Generally the primary band is caudad shifted compared with the 1582 cm^{-1}G point frequency which is the central area maximum of highest optical branching of graphite, and even 1563 cm^{-1} may fall depending on heating by a laser beam. In the lowest laser output, a nanotube produces a spectrum similar to microcrystal graphite. A weak band [in / in another remarkable feature / about 1350 cm^{-1}], almost -- 2700 cm^{-1} (1350 cm^{-1}) -- and -- The secondary feature in 3248 cm^{-1}, and 1350 + It is in combination mode in 1600 = 1950 cm^{-1}. this invention person found out the spectral characteristics same about all the MWNT(s). The spectral characteristics

are approximated with the spectrum acquired from the graphite-electrode material which performed detailed base processing (drawing 3). the G band (1579 cm^{-1}) of a nanotube -- the maximum -- most -- the overall width (FWHM) in a value being about 28 cm^{-1}, and, On the other hand, in microcrystal graphite (1580 cm^{-1}), it is 18 cm**-1**, and is 14 cm^{-1} in graphite (1581 cm^{-1}). This result has agreed with the observation of TEM which showed that it was not a perfect crystalline substance, although the character of the nanotube resembles graphite extremely. The relative intensity of the Raman band measured with the nanotube by which hydrothermal generation was carried out shows that it has the same degree of perfection as the nanotube generated at 4000 ** in accordance with what was obtained using arc discharge process.

[0022]Since a nanotube oxidizes quickly in the air, it can be easily cut by the laser beam of maximum strength. This point is convenient to open the closed tube or to cut them in size suitable for various kinds of application.

[0023]** **: Some growth mechanisms which change according to the synthetic art of a carbon nanotube are provided so that the outline of Ebbesen may see. The analysis of the shape (drawing 2) of a nanotube supports the open end growth mechanism which provides an active site for the atom located in the open end of graphite structure to capture carbon from a hydrothermal fluid. However, existence of the closed tube containing nickel has suggested a possibility that many mechanisms will act in [of one] supercritical fluid. It is shown that it is barred that a two-layer nanotube stops and closes the result of molecular mechanics research in the metastable energy minimum state. Closing of a nanotube can be generated by the five membered ring which produces the geometry which curves in a tip. The nanotube can grow, when the six membered ring of carbon, a five membered ring, and eight membered-rings add around an open tube end. Since hydrothermal environment has CH_4 and CO in solid carbon and an equilibrium situation under hydrothermal synthesis conditions excluding aromatic hydrocarbon, it can consider growth of the nanotube from these kinds. The thickness of a carbon nanotube increases with island growth of the graphite base surface on the outside surface of the tube which grows. Some separate models are led about catalysis growth of the carbon nanotube (decomposition of acetylene by a metal catalyst, etc.). The RASEN growth mechanism depending on a parameter assumes [a globular shape, conical shape, or] that this invention person brings about

the growth pattern of a parallel layer mostly.
[0024]Since it has a broad crevice, a hydrothermal nanotube is interesting as micro and a nano fluid device, and a chemical processing plant on a chip. Micro / nano fluid study is one field with very promising new micro engineering. MWNT(s) of the same diameter (33 nm) of the range as the thinnest thing of the nanotube of this example are the Young's modulus of 1.8TPa, and 14.2 (it is proved that it has the flexural strength of 8GPa, therefore it has a microfluid and a promising possibility to application of MEMS.). Since the chamber or crevice between nano sizes cannot be made from a photolithography with a limit according to the feature of abbreviation 1 - mm, it is necessary to use a nano pipe for making a nano fluid device possible. Probably, use of a nanotube will be effective also in generation of the cylindrical channel optimal for laminar flow. The interconnection during a nano fluid chip or the interconnection between a chip and an analysis object (for example, cell) also becomes possible using a nano pipe.
[0025]The hydrodynamics in a nano-scale is not developed enough yet, but there is also little experimental data. However, it is known by capillary force that a fluid can be attracted with a nanotube. Generally, the inside diameter of a carbon nanotube is 10 nm or less, and since the wall thickness is over the inside diameter, only few portions of a section can use it for a fluid application channel. Within a several nanometers opening, it is concluded that the interaction of the molecule of a fluid and the wall of a nanotube is strong, and it is impossible to penetrate and for anythings to flow. The nanotube of the inside diameter smaller than 4 nm could not be filled with salt melt. The beam of a size only becomes quite small and the hydrothermal tube (drawing 2) is far similar with the pipe currently used in the macro world. About 100-nm channel enables flowing through of a fluid. If metal is filled, the nanowire of size and the same axle-like nano cable which can suit a next-generation electron device and MEMS will be formed.
[0026]Unlike MWNT generated in a vacuum or under ambient pressure, the closed hydrothermal nanotube contained the fluid of the water base by which the encapsulation was carried out under the pressure (drawing 2 C). The capability to hold pressurizing fluid even at the time of heating by the bottom of the high vacuum (10^{-8}torr) in the capability to function as a minute pressure container which a hydrothermal nanotube has, and also TEM, and an electron beam makes the perfection of sufficient, very high

intensity for technological application, and a wall check. This also hangs down a unique opportunity to action research of the fluid in a nano size channel, and the analysis of the aquosity sample in TEM.

[0027]Recently, the fullerene formed under denaturation hydrothermal environment was discovered in the pit in China. This result means the possibility of formation of the carbon nanotube in a nature. Since the formation conditions of the coal burying layer include the hydrothermal-reaction process in low or the intermediate temperature in a pressure of a degree in the middle, they can expect that a nanotube will exist in coal or a natural hydrothermal graphite burying layer.

[0028]Composition by the autoclave of the nanotube under hydrothermal-reaction conditions was proved by this example. The hydrothermal synthesis of a carbon nanotube will change the method by which the present nanotube is produced, and gives more environment-friendly art (the system of the closed water base [in / middle / the temperature and the pressure of a degree], low energy expenditure, and high yield). If the formation mechanism of the nanotube under hydrothermal-reaction conditions is understood more clearly, optimization of the conditions for growing up a lot of MWNT(s) should be attained. If the inside diameter of a nanotube becomes large and growing temperature becomes low, closing of a nanotube will be prevented and it will be expected that growth of a long nanotube is attained. Probably, it changes possible with inclined type autoclave [need / to be grown up / while a very long carbon nanotube controls / to enable one-dimensional growth under concentration or a temperature inclination]. This method is promising for producing the nanotube of several pounds Nissan, if commercial mass autoclave is used.

[0029]The action of C_{60} under example 2 hydrothermal-reaction conditions: Formation and the geological meaning of stability and a carbon nanotube [0030]Here, in the geological environment of the temperature between 200 ** and 800 **, and the pressure of 100 or less MPa, reference is made about the action of C_{60} according to the absence and existence of nickel under general hydrothermal-reaction conditions. The stability of C_{60} and the range of decomposition under existence of a hydrothermal fluid were checked, and formation of the carbon nanotube under existence of a nickel particle was shown. The result of research by this invention person explains existence of the natural carbon nanotube in the field of the earth crust of the

earth influenced by the hydrothermal-reaction system, and the absence of the fullerene in the rock exposed to the hot aquosity fluid.

[0031]Fullerene (C_{60}) powder (99.95% of purity, Science Laboratories Co., Japan) was used in all the experiments. After putting the small-quantity sample (>>0.020g) of this fullerene powder in gold capsules (capacity >>0.1-0.2-cm^3) 3 mm in diameter, double distilled water (>>0.3g) was filled to the capsule. Subsequently, after sealing the capsule and putting into autoclave (Tuttle Books Roy (Tuttle-Roy) type), it heated from 20 minutes at 200 ** of periods of 48 hours, 400 **, 500 **, 600 **, 650 **, 700 **, 750 **, and 800 **. Nickel powder (99.8% of purity, Nilaco Co., Japan) was added to some capsules in 3% of the weight of quantity. 168 hours heated the capsule in which the quantity of water contains nickel which was 30%-100% of solid phase (weight) at 400 **, 500 **, 600 **, and 700 **. a sample substance -- Tokyo Institute of Technology -- Raman spectroscopic analysis and an X diffraction (XRD) -- feature analysis was conducted in the University of Illinois research resource center of U.S. Chicago with the field emission scanning electron microscope (FESEM) and the transmission electron microscope (TEM).

[0032]The Raman spectrum selected among the fullerene powder processed in hydrothermal is shown in drawing 4. The Raman spectrum which expressed "the put-in state" is equivalent to the fullerene powder which did not perform water heat treatment. This spectrum is a characteristic spectrum of C_{60} and is ten Raman activity modes. All

(1996) of [Dresselhaus, M. S., Dresselhaus, G. & Eklund, and P. C. "Raman scattering in fullerene" J. Raman Spectrosc.27 and 351-371] are shown clearly. The spectrum of C_{60} obtained after carrying out water heat treatment into

pure water at 200 ** - 400 ** (0.3 hour - 48 hours), Hydrothermal-reaction conditions [in / it is almost equivalent to the spectrum of C_{60} of the put-in state, and /

the above-mentioned temperature requirement and the above-mentioned time] show that it was stable (drawing 4). Although it is 500 ** (168 hours) or a higher temperature, shorter time, For example, in addition to a band peculiar to C_{60} becoming weaker, a new band appeared in the Raman

spectrum obtained from 600 ** or (18 hours) the fullerene processed in hydrothermal at 700 ** (0.3 hour). Two strong wide bands in about 1335-cm^{-1} and 1608-cm^{-1} originate in amorphous carbon. [GOGOTSI, Y.G. & Yoshimura, and M.

"formation of carbon film on carbide under hydrothermal-reaction conditions" Nature367,628-630 (1994)] .The position of these bands (D band of a lower part shift and the G band of an upper part shift) of amorphous carbon is typical about the carbon by which hydrothermal formation was carried out. The origin is unknown although the shoulder belt is observed by the position of about 1200-cm^{-1} in the carbon by which hydrothermal formation was carried out. It is proved after the water heat treatment at 600 ** (48 hours), 700 ** (168 hours), or 800 ** (0.3 hour) that the Raman spectrum did not show any fullerene, either but C_{60} had disassembled it thoroughly (drawing 4). The XRD pattern of the fullerene powder which performed water heat treatment had agreed with the Raman spectrum well. The new broad peaks which show decomposition of fullerene are about 24.5 degrees and 43.5 degrees, and it was thought that these originated in graphite-like carbon (drawing 5 b). It is shown that C_{60} fullerene disassembles gradually both the Raman spectra and XRD patterns of C_{60} by which water heat treatment was underwater carried out under a different condition as the temperature and time of water heat treatment increase. After processing of a length of 48 hours under the pressure of 100MPa, the maximum temperature in which C_{60} fullerene has stability was 400 **.

[0033]Although C_{60} crystal was changed into amorphous carbon during water heat treatment, without shape changing remarkably (drawing 5 a) and the part was graphite-ized (drawing 5 b), there were some which have an etching base which is a foregone conclusion. The FESEM analysis of the fullerene crystal after the water heat treatment under existence of nickel showed that the carbon nanotube was formed near the Ni particle (drawing 6 a). The multiwalled carbon nanotube had a circular section, the outer diameter was generally the range of 30 to 40 nm 30 to 120 nm, and wall thickness was 5 nm (drawing 6 b). The wall thickness of a carbon filament is the range of four to 40 nm, and this supports ten to 100 graphite layers. In the wall of a nanotube, although TEM of high resolution has gathered well, it shows the graphite layer which is not an ideal-like (drawing 6 b). The relation which the tube to a nickel particle is obvious, or was generally consistent was not accepted. Only very few nanotubes contained nickel nano particle at the tip. In some cases, the lattice fringe inclined to the vertical axis of a tube, and had produced RASEN nature.

[0034]The important meaning acquired from a result here is the possibility of the hydrothermal synthesis of a carbon nanotube. Hydrothermal art usually gives the output which has far high homogeneity and has yield (quick growth rate) higher than a gas or vacuum treating rather than based on solid processing. Various kinds of broad combination exists in a solvent / solute system. [Eckert, C. A., Knutson, B. L. & Debenedetti, P. G. "supercritical fluid as chemicals and a solvent for substance processing", Nature 383, 313-318 (1996), Yoshimura, M. & Byrappa, and K. "Hydrothermal art for crystal growth and substance processing", (Andrew Williams and Noyes Inc., New Jersey, U.S., 2000) Issue] . Probably, a direction besides the liquid from a point of restoration of output, transportation, mixing, and/or separation will be advantageous. [Yoshimura, M. & Byrappa, K. "hydrothermal art for crystal growth and substance processing" (Andrew Williams and Noyes Inc., New Jersey, U.S., 2000), issue] .The fluid conforms to the circulation / recycle, and substance processing in a closed system thoroughly. Furthermore under a hydrothermal-reaction condition, especially a fluid gives diffusion, adsorption, reaction velocity, and the possibility of acceleration of crystallization (nucleation and growth). [Hydrothermal technical" (Andrew Williams and Noyes Inc., New Jersey, U.S., 2000) for Yoshimura, M. & Byrappa, K. "crystal growth, and substance processing, issue] .Under the supercritical state, the fluid has a part of strong point of both a fluid and a gas. Since the diffusion in supercritical fluid is higher than it can set into a fluid and viscosity is low, mass transport of wave increases. [Supercritical fluid" as Eckert, C. A., Knutson, B. L. & Debenedetti, P. G. "chemicals, and a solvent for substance processing, Nature383, and 313-318 (1996)] .

[0035]It proves [nanotube] that it can form under hydrothermal-reaction conditions, and this invention has suggested the possibility of a carbon source with lower complexity. On the large-scale of a carbon nanotube, composition of low temperature, i.e., low cost, will be one big step towards broad application of these substances. The common carbon nanotube in which the nanotube of this invention is formed by a carbon arc electric discharge method (being a two to 25 nm diameter usually one to 3 nm internal diameter of hollow) [Ebbesen, T. W. "carbon nanotube" Ann. Rev. Mater. Sci. 24, and 235-264 (1994)] A twist is also slightly thick and it has a central larger blank than it. The quality of the nanotube of this invention shows a possibility that the unique kind of carbon allotrope by hydrothermal art will be compoundable, and this is another

advantage of a hydrothermal crystallization method. [0036]On the other hand, the result of this invention also has the meaning on very important geology. The hydrothermal solution which has the temperature [it fully exceeds 50 degrees and 500 **] of a between is distributed generally within the earth crust of the earth, and widely. [Pirajno, F. "hydrothermal mineral burying layer" (Springer-Verlag, German country Berlin Hy Dell Berg, and 1992)], .The hydrothermal fluid which circulates through the bottom of the surface of the earth oozes, and is involved in various geological processes by transportation, precipitate of those mineral components, or hydrothermal deterioration of the existing mineral. [Pirajno, F. "hydrothermal mineral burying layer" (Springer-Verlag, German country Berlin Huy Dell Berg, 1992)], .It depends for the conditions of hydrothermal activity on the kind of hydrothermal system. For example, in the case of a hydrothermal system by a meteorite, temperature does not usually exceed 400 **, but in the case of a hydrothermal system of a submarine floor, it becomes with the range over 350 to 500 **. [Pirajno, F. "hydrothermal mineral burying layer" (Springer-Verlag, German country Berlin Huy Dell Berg, 1992)], .Especially the hot hydrothermal activity that will be about 1000 ** is connected with the denaturation and the magma system which contain H_2O as main volatile fluid. [Pirajno, F.

"hydrothermal mineral burying layer" (Springer-Verlag, German country Berlin Huy Dell Berg, 1992)], . [0037]The experiment of this invention using C_{60} was seen

from the geological scale, and was carried out in very short time (it compares with the old period in the case of a geological process, and is only several hours). Nevertheless, the fullerene was not able to bear the water heat treatment in a temperature higher than 400 **. fullerene -- H_2O -- it is

nothing, and in order to show stability in an elevated temperature extremely, this deserves surprise. Molecular mechanics research shows that it becomes unstable, if C_{60}

exceeds 4000 ** at least. [-- Zhang -- B . -- L . -- Wang -- C . -- Z . -- Chan -- C . -- T . -- & -- Ho -- K -- M . -- "-- carbon -- fullerene -- thermal -- collapse -- " -- Phys . -- Rev . -- B -- 48 -- 11381 (1993) --] .It is shown that fullerene decomposes the experiment using C_{60} crystal into

amorphous carbon at 700 ** - 950 ** into an inert atmosphere. [Stetzer, M. R., Heiney, P. A., Fischer, J. E. & McGhie, A. R. "thermal stability of solid C_{60}", Phys. Rev. B

55, and 127-131 (1997)] .However, the result of this

invention shows that pure water promotes decomposition of fullerene strongly. Since this process is controlled dynamically, if the time of water heat treatment becomes long far, it will be expected that the range of stability moves to the direction of a lower temperature. The result of this invention will explain the reason which does not try to be [fullerene] rare. That is, the reason not only needs to be exposed to the extreme conditions in which the rock containing carbon rarely occurs, but there is C_{60} in

hydrothermal stability being low. Formation of the carbon nanotube under hydrothermal-reaction conditions is a field in the earth crust of the earth influenced by a hydrothermal fluid, and means the possibility of the existence of the natural carbon nanotube in the rock which contains carbon abundantly. Although it seems that a fullerene mine does not go beyond the science fiction in addition, discovery of the large-scale natural nanotube burying layer is approaching actually. [Finishing [Osawa, E. et al. "observation of the fullerene in coal and carbonaceous rock, a carbon nanotube, and a nano particle", Nature, and presentation] (1999)] .

[Translation done.]